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Observation of Fractional Stokes-Einstein Behavior in the Simplest Hydrogen-Bonded Liquid

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Quasielastic neutron scattering has been used to investigate the single-particle dynamics of hydrogen fluoride across its entire liquid range at ambient pressure. For $T > 230$ K, translational diffusion obeys the celebrated Stokes-Einstein relation, in agreement with nuclear magnetic resonance studies. At lower temperatures, we find significant deviations from the above behavior in the form of a power law with exponent $\xi = -0.71 \pm 0.05$. More striking than the above is a complete breakdown of the Debye-Stokes-Einstein relation for rotational diffusion. Our findings provide the first experimental verification of fractional Stokes-Einstein behavior in a hydrogen-bonded liquid, in agreement with recent computer simulations [S. R. Becker *et al.*, Phys. Rev. Lett. **97**, 055901 (2006)].

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Our current view on the diffusive motions of a tagged spherical particle within a liquid pictures it as executing random walk movements characterized at long times by a diffusion coefficient given by Stokes' law [1],

$$D = \frac{kT}{C\eta r}, \quad (1)$$

where r stands for the particle radius, T the temperature, C a constant whose value depends on the boundary conditions imposed on the surface of the particle (6π for so-called "stick" and 4π for "slip" boundary conditions), and η the macroscopic shear viscosity.

Given the approximations involved in the derivation of Eq. (1), its predictive capabilities to deal with experimental data for simple liquids in their normal liquid ranges is both surprising and intriguing [2]. Likewise, an understanding of the deviations from this simple behavior and how these relate to the underlying microscopic dynamics constitutes an active area of research, particularly within the context of supercooled and glass-forming liquids [3].

Our present communication was motivated by recent computer simulation results from Becker *et al.* [4] which report on the emergence of fractional Stokes-Einstein (SE) and Debye-Stokes-Einstein (DSE) behavior in a prototypical model of a network-forming liquid. SE and DSE were used to denote the obedience of the translational and rotational diffusion coefficients to Eq. (1), respectively. By fractional SE and DSE, the authors report on the finding of a power-law dependence of D vs η/T with exponents ξ well below the expected $\xi = -1$. Here we provide direct experimental scrutiny of the computer simulation results by means of a quasielastic neutron scattering (QENS) study carried out on liquid hydrogen fluoride (HF). This fluid is composed of linear molecules which display the strongest hydrogen bond (HB), evinced by an interaction

energy per molecular pair of ~ 250 meV. In contrast to other hydrogen-bonded liquids (HBL's) such as water and the lower alcohols, HF may be regarded as the simplest HBL. In fact, its simple molecular shape and the strength of the HB interaction allows the separation of translational and rotational contributions to the measured differential cross section, thus enabling us to determine robust estimates for the two transport coefficients. In stark contrast with the abundant literature on theoretical and simulation studies [5], the aggressive nature of this material has largely hampered detailed experimental corroboration of most simulation results. Only recently, predictions regarding its static structure or dynamical properties have been confronted with experiment by means of neutron scattering [6,7].

Experiments were carried out using the QENS-IPNS [8] and the IRIS-ISIS [9] spectrometers. These two QENS instruments enabled access to relatively narrow energy ranges with high resolution (-200 – 1000 μ eV, $\Delta E = 9$ μ eV on IRIS-ISIS), as well as a broader energy-transfer range at the expense of a lower energy resolution (± 1500 μ eV, $\Delta E = 45$ μ eV on QENS-IPNS). Such a combination provided a stringent cross-check to ensure that the separation of quasielastic components was not affected by the finite extent of the instrumental energy windows. For sample preparation, an identical procedure to the one used in recent work by some of us [7] was also followed herein. Annular-geometry cells were manufactured from Monel (Alloy 400) and surface passivated under an atmosphere of fluorine gas [10]. A sample thickness of 0.50 mm was chosen in order to minimize excessive beam attenuation as well as absorption and multiple-scattering effects. We also performed quick runs across the melting point ($T = 170$ – 205 K). The observation of a sharp and distinct drop in elastic-line intensity at $T = 190 \pm 1$ K

provided an upper limit for the presence of H₂O of <0.5% mol [11].

A representative set of QENS spectra is shown in Fig. 1. Significant spectral broadenings of the narrower QENS peaks are apparent in these data. Under the incoherent approximation [12], this behavior is indicative of translational diffusion. In addition, a second yet much broader QENS component extending a few hundred μeV is also present but its energy width remains relatively constant with Q , e.g., a localized or rotational mode. The observed order-of-magnitude differences in energy widths for the two QENS modes prompted us to fit these data without explicit recourse to any particular model for the underlying translational and rotational motions. To this end, a Bayesian algorithm was used to find the highest number of Lorentzian modes supported by the experimental data [13]. As shown in Fig. 1, this procedure amply justifies the

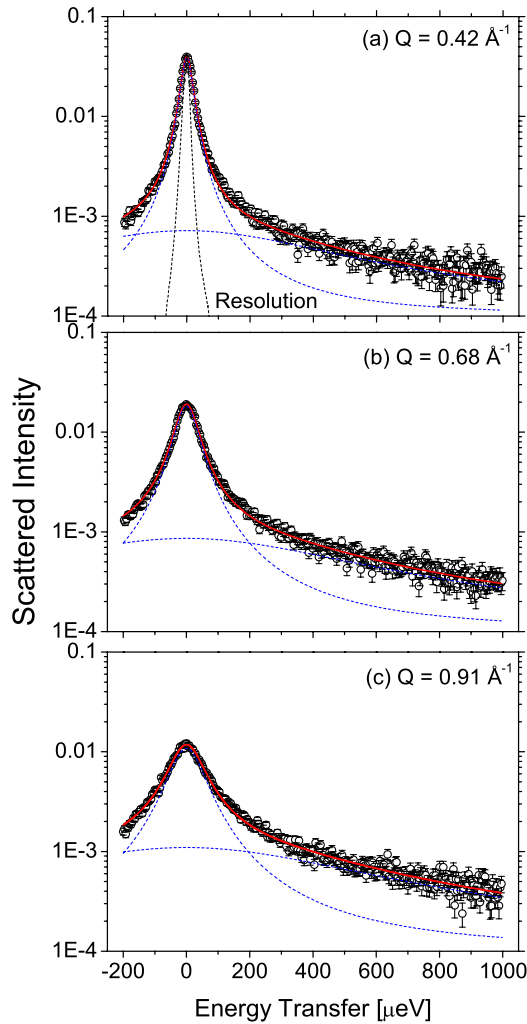


FIG. 1 (color online). QENS spectra at $T = 195$ K measured on IRIS-ISIS. Fits are shown in red (or gray) and individual Lorentzian components in dashed blue (or dark gray). In all cases, the instrumental resolution has been folded into our Lorentzian model for the purposes of fitting.

presence of two Lorentzian components and provides an excellent description of the experimental data.

Figure 2 presents the narrow QENS widths obtained by use of the aforementioned fitting procedure. For all temperatures investigated, the experimental data obey a jump-diffusion-type mechanism of the form

$$\Gamma_T(Q) = \frac{D_T Q^2}{1 + \frac{D_T Q^2}{E_0}}, \quad (2)$$

where Γ_T is the observed Lorentzian energy width (HWHM), D_T is the translational self-diffusion coefficient, and E_0 is related to a mean residence time τ_0 between diffusive jumps via $\tau_0 = \hbar/E_0$ [14]. In Fig. 2, we have chosen to show this expression in linearized form in order to highlight our ability to distinguish between D_T (inversely proportional to the slope) and E_0 (inversely proportional to the intercept).

Figure 2(b) shows D_T as a function of temperature. Our results are compared with those obtained by pulsed-field-gradient nuclear magnetic resonance (PFG-NMR) [11]. Our QENS data reproduce the PFG-NMR diffusion coefficients at high temperatures. For $T > 230$ K, we obtain an Arrhenius activation energy $E_A = 103 \pm 8$ meV [black solid line in Fig. 2(b)], in close agreement with a PFG-NMR value of 102.8 meV. However, significant deviations are apparent at lower temperatures, QENS data being con-

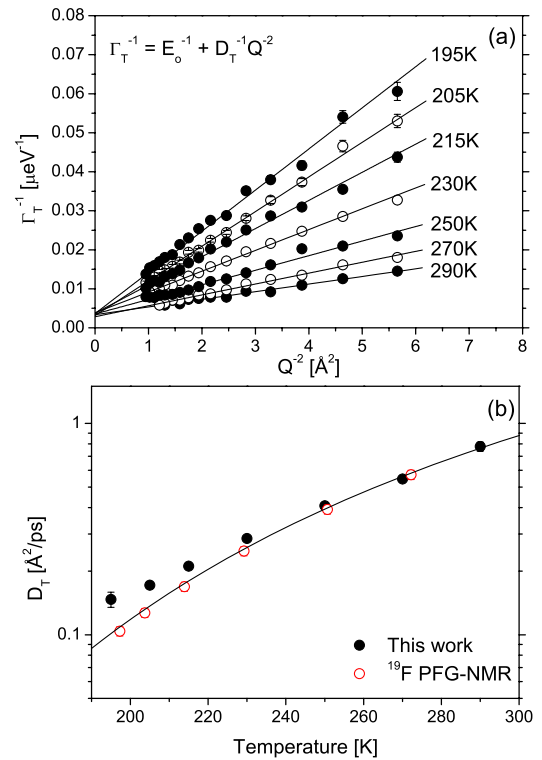


FIG. 2 (color online). (a) Inverse QENS energy widths for the translational mode as a function of momentum transfer (IRIS-ISIS); (b) temperature dependence of the translational self-diffusion coefficient and comparison with PFG-NMR results.

sistently higher than PFG-NMR. These differences could arise from a number of different reasons such as differences in sample purity. Notice, however, that the Fickian behavior followed by the translational linewidths down to the lowest explored temperatures ensure its pure mass-diffusion character. Furthermore, as we shall see below, the separation in linewidths becomes more marked as the temperature decreases so that our estimates for the translational diffusion coefficients become more accurate at the temperature decreases down to freezing.

Further analysis of the scattered intensities provides additional insight onto the physical origin of the observed spectra. To this end, Fig. 3 shows the total intensity of the translational mode as a function of Q along with a fit using

$$I(Q) = e^{-(1/3)u^2Q^2} j_0^2(QR) \quad (3)$$

where the first term is a Debye-Waller factor with mean displacement u , $j_0(QR)$ is the zeroth-order spherical Bessel function, and R is the radius of rotation. Equation (3) has been derived by considering a dynamic structure factor $S(Q, \omega)$ of the form $T(Q, \omega) \otimes R(Q, \omega)$ where $T(Q, \omega)$ and $R(Q, \omega)$ correspond to translational and rotational modes and \otimes denotes a convolution product. Further, $R(Q, \omega)$ assumes isotropic rotational diffusion [15]. A mean displacement of $u = 0.47 \pm 0.04$ Å was obtained from independent measurements in the crystal phase at $T = 170$ K. It matches closely that of 0.46 Å reported by Axmann *et al.* [16]. Likewise, we find $R = 0.88 \pm 0.05$ Å, in excellent agreement with that expected for HF, namely, $R = (m_F/m_{\text{HF}})R_{\text{HF}} = 0.89 \pm 0.03$ Å, where $R_{\text{HF}} = 0.94 \pm 0.03$ Å has been taken from the neutron diffraction study of McLain *et al.* [6]. Thus, our analysis provides a direct link between the geometry of the HF molecule and its dynamical radius of gyration. Within the remit of the model for $S(Q, \omega)$ presented above, rotational diffusion at small energy transfers is char-

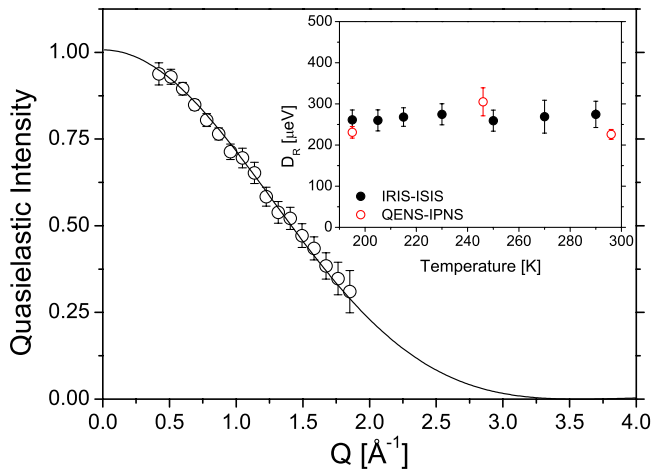


FIG. 3 (color online). QENS form factor ($T = 195$ K). The inset shows the temperature dependence of D_R (see text for details).

acterized by a Lorentzian line shape of width $\Gamma_R(Q) = \Gamma_T(Q) + 2D_R$, where D_R is a diffusion coefficient related to the characteristic rotational correlation time τ_R via $D_R = \hbar/6\tau_R$. This expression arises from the leading term of the Sears expansion for rotational diffusion [15]. Given our value of $R \sim 1$ Å, this assumption is well justified as higher-order terms proportional to $j_l^2(QR)$ ($l > 2$) have a negligible contribution ($< 10\%$) over our energy and momentum ranges. D_R 's for HF were then obtained as a function of temperature by taking explicit account of the previously determined translational QENS widths $\Gamma_T(Q)$. The inset in Fig. 3 shows the result of such a procedure for experiments carried out on both spectrometers. Surprisingly, these data do not show an obvious dependence with temperature, yet it is reassuring that the same results have been obtained by two independent measurements. A microscopic explanation for this unusual behavior is beyond the scope of the present Letter, but it should be noted that HF displays the largest known rotational constant after molecular hydrogen ($B_{\text{HF}} \sim 21$ cm $^{-1}$) [17] as well as dynamic and kinematic viscosities 4–5 times smaller than those of water at ambient temperature.

The validity of the SE and DSE relations as a function of temperature is tested in Fig. 4 using the macroscopic viscosities of Simons *et al.* [18]. For translational diffusion, the low-temperature data follow a power-law exponent $\xi = -0.71 \pm 0.05$ with a crossover to SE behavior above 230 K. For rotational diffusion, the power-law exponent approaches zero within experimental error ($\xi = -0.02 \pm 0.04$). The observed behavior is very similar to what has been extracted from computer simulations of the ST2 model of water by Becker *et al.* [4]. There, translational

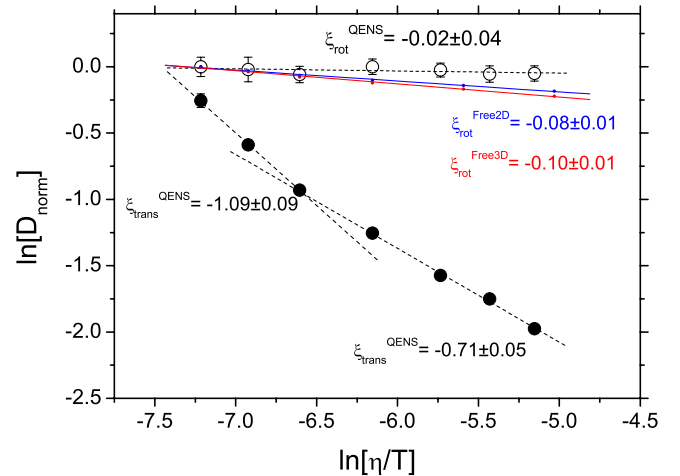


FIG. 4 (color online). Log-log plots of QENS diffusion coefficients vs η/T (data in black circles; open: rotational; solid: translational). SE and DSE behavior is characterized by a power-law exponent $\xi = -1$. For the purposes of comparison, diffusion coefficients have been normalized by their corresponding high-temperature values ($T = 290$ K). Red (or gray) and blue (or dark gray) lines show τ_{free}^{-1} for freely rotating HF in two and three dimensions.

diffusion was shown to deviate from the SE relations with power-law exponents $\xi \approx -0.8$, and was largely independent of density. Moreover, it was also found that rotational motion experienced a more dramatic enhancement than translational diffusion, leading to power laws with $\xi \approx -0.25$. Based on our experimental results, liquid HF displays an even more pronounced breakdown of the DSE relation than that found for ST2 water. This behavior is largely different from observations in other liquids, e.g., water, where rotational diffusion follows the Arrhenius relation and activation energies approach librational frequencies. It is also indicative of a strong decoupling of HF rotational motions from the surrounding medium. To illustrate this point further, Fig. 4 shows the temperature dependence of the inverse rotational period τ_{free}^{-1} for an ensemble of isolated HF molecules. It has been obtained by considering the root-mean-squared angular momentum $J_{\text{rms}} = \langle J^2 \rangle^{1/2}$ and the classical relation $\tau_{\text{free}}^{-1} = B_{\text{HF}} J_{\text{rms}} / \hbar$ for the cases of two- and three-dimensional rotation. Whereas it is likely that this simple model cannot describe accurately the complexity of stochastic rotational motions in liquid HF, it does serve to illustrate a plausible mechanism for strong departures from the (expected) Arrhenius-like dependence of microscopic transport coefficients. Similar free-rotor-like behavior has also been observed for HF in noble-gas matrices [19]. Moreover, the residence time τ_0 exhibits a similar invariance with temperature, as demonstrated by the common intercept to all curves shown in Fig. 2 with $\tau_0 \sim 2.5$ ps. The picture that emerges from the present study suggests that fast and almost free rotations ($\tau_R \sim 0.4$ ps) take place within a temporal lapse τ_0 which could tentatively be thought of as the time needed for a molecule to bind to a nearest neighbor. It would be insightful to see whether molecular-dynamics simulations using a realistic description of the inter- and intramolecular modes in HF can establish a link between the emergence of fractional SE and DSE behavior and the presence of solid-like excitations in this seemingly simple HBL, as recently observed via inelastic neutron scattering [7].

In summary, the present Letter provides experimental evidence of fractional power-law departures from the SE and DSE relations in a liquid. Departures from the DSE relation are strong and provide a vivid reminder of the ability of molecules to execute rapid reorientational motions in media of very large viscosity, such as some molecular (rotator-phase) crystals [20]. Our findings emphasize the growing importance of the finite shape of molecules adjacent to the one executing Brownian-type motions as the temperature is decreased. Under such circumstances, the shape and interactions with neighboring particles do matter and the inclusion of “wetting” or “sticking” conditions would make the description of the transport coefficients in terms of the macroscopic viscosity even poorer. A theory in the same spirit as those of Hill, Gierer, and Wirtz [21] which emphasize the temperature dependence of molecular interactions would pave the way

to further progress in our understanding of the phenomena here described.

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